JOURNAL

OF THE

WASHINGTON ACADEMY OF SCIENCES

VOL. VII FEBRUARY 4, 1917 No. 3

PHYSICS.—*Standard substances for the calibration of viscometers.*[1] EUGENE C. BINGHAM and RICHARD F. JACKSON, Bureau of Standards. (Communicated by C. W. Waidner.)

For the calibration of viscometers there is a need for one or more liquids which can be easily obtained in pure condition, and which have viscosities that are greater than that of water and that are known with a considerable degree of certainty. The substances selected are mixtures of ethyl alcohol and water, and sucrose and water. Previous work upon water and alcohol being adequate, the present experiments were confined to sucrose and water. The sucrose was purified by repeated recrystallization from water solution, and contained residual impurities of the order of one-thousandth of a per cent. The compositions of the solutions used in the measurements were determined by density measurements and by polariscopic tests.

The viscometer used in the investigation consisted essentially of a U-tube fitted with a capillary limb surmounted by a bulb with constrictions. The bulb served as a measure of the volume of liquid forced through the capillary. A bulb of similar size and shape was sealed on the other limb. The viscometer was connected to a manometer and an apparatus for the application

[1] To appear in detail as Bureau of Standards Scientific Paper No. 298.

of pressure. From the observations the viscosity was calculated by the usual formula:

$$\eta = Cp\tau - C'\frac{\rho}{\tau}$$

in which η is the viscosity, p applied pressure, ρ density of liquid, τ time of flow, C and C' constants abbreviated from the complete viscosity formula. C' was found by direct calculation, C by measuring the time of flow of pure water at 20°C. The viscosity of water at 20°C. was taken as 0.01005.

The viscosity was measured at a variety of applied pressures. To obtain the true effective pressure, the height of liquid in the manometer was corrected for air buoyancy, column of connecting air, and hydrostatic head of the liquid undergoing measurement. In order to be certain that the drainage of the solution was complete, both the time of flow required to empty and that to fill the bulb were measured. Furthermore, the viscosity was found to be independent of applied pressure. To test the calculations and corrections the viscosity of water was measured over a considerable range of pressures. The value was found to be constant.

In order to avoid the arbitrary scales of commercial viscometers and the inconvenient magnitudes of the absolute units, we suggest the use of the "centipoise" as a unit of viscosity. This is the one-hundredth part of the c.g.s. absolute unit. The centipoise is almost exactly the viscosity of water at 20°C. (0.01005) and, hence, is at the same time the specific viscosity of any substance referred to water at very near 20°C.

The existing data for the viscosity of water have been reviewed in order to obtain a value as far as possible in accord with our present knowledge. The mean value expressed as fluidity is given by the formula:

$$\phi = 2.1482\left\{(t-8.435) + \sqrt{8078.4 + (t-8.435)^2}\right\} - 120$$

in which ϕ is the fluidity, and t the centigrade temperature.

The fluidities of mixtures of ethyl alcohol and water expressed as functions of the temperature, and of the weight and volume percentage of alcohol, will be given in the detailed paper.

The viscosity of a 39.99 per cent sucrose solution was measured at temperatures varying from 0°C. to 95°C. The observed values correspond to the formula:

$$t = 0.597\ (\phi + 20) - \frac{1438.6}{\phi + 20} + 38.24$$

On repeating these measurements practically the same values were obtained.

Measurements were made with 20.007 per cent and 59.96 per cent sucrose solutions also. The fluidities at the latter concentration correspond to the formula:

$$t = 1.472\ (\phi + 5) - \frac{323.2}{\phi + 5} + 58.62$$

The values found in the present investigation indicate a higher viscosity than those of previous investigators.

CHEMISTRY.—*Some problems of the oxides of iron.*[1] ROBERT B. SOSMAN, Geophysical Laboratory.

Starting with the general principle that the soundest progress in science is made by proceeding from that which is simple and understandable to that which is more complex and less understandable, various investigators have sought to unravel the complexities of natural rocks and minerals by studying first their simplest constituents. Since it appears that under most rock-forming conditions silica (SiO_2), alumina (Al_2O_3), lime (CaO), and magnesia (MgO) always act as units, these oxides may be taken as the pure components in the fundamental experiments.

With the oxides of iron the case is different. The equilibrium between ferrous and ferric iron in a mineral or rock can vary with every change of temperature and with every change in the amount or pressure of available oxygen. In order to under-

[1] Presidential address, Chemical Society of Washington, January 11, 1917. Presented before a joint meeting of the Chemical Society and the Washington Academy of Sciences.

stand ferrous silicate and the minerals in which it occurs, therefore, we must go back one step further, and study the system iron-oxygen.

THE PHASE-RULE DIAGRAM OF THE SYSTEM IRON-OXYGEN

The logical point at which to begin a survey of the pressure-temperature-concentration relations in the two-component system iron-oxygen is with the pure component iron. We have learned a great deal in recent years about the properties of pure metallic iron, although the difficulty of preparing the metal quite free from its usual impurities of carbon, hydrogen, sulphur, phosphorus, manganese, and silicon, has delayed the determination of its elementary constants.

But when we add oxygen, the second component, to the system we come into a little-known region which extends as far as the compound Fe_3O_4. The solubility of oxygen in solid iron is certainly not large, but has not been accurately determined. Austin[2] states that the oxygen found by analysis of iron bars does not exceed 0.29 per cent, and that the most of this seems to be in the form of oxide films in mechanical admixture. Pickard[3] concludes from his analyses that 0.092 per cent of oxygen is soluble in liquid iron as FeO, although a part of this may separate out on the solidification of the metal. It is thus evident that there is no extensive solid solution of oxygen in iron. But the small quantity that is present has a very large influence, especially on the magnetic properties of the metal, as appears from the work of Yensen.[4]

The next question is, what is the lowest oxide in equilibrium with metallic iron? Ferrous oxide, FeO, has been generally assumed to be the oxide lowest in oxygen, but the data concerning it are far from satisfactory. Various methods for preparing FeO are found in chemical literature. Mr. Hostetter and I have tried several of these, and our experience has invariably

[2] Engineering, **100**: 455. 1915.
[3] Iron Age, **98**: 184–186. 1916.
[4] YENSEN, T. D. Univ. Illinois, Eng. Exp. Station, Bulls. 72, 77, 83. 1914–1916.

been that the product was a mixture of iron (or iron carbide) with magnetite or with some oxide intermediate in composition between FeO and Fe_3O_4. The best work on FeO has been that done by Hilpert, and his conclusion, likewise, is that the various methods commonly cited do not yield FeO, although the product sometimes has an average composition nearly equivalent to the composition FeO.

Hilpert and Beyer[5] found that by reduction of Fe_2O_3 by hydrogen saturated with water vapor they could obtain products which were richer in ferrous iron than Fe_3O_4, but which contained no metallic iron. The higher the temperature of reduction, the higher the percentage of "FeO." A product containing only 1.5 per cent of Fe_2O_3 was obtained by reduction at 1100°; at 700° the upper limit was 85 per cent of FeO. The reaction velocity is so slow, as equilibrium is approached, that it is difficult to say what the final solid phases would be. Hilpert believes that solid solutions exist between Fe_3O_4 and FeO, perhaps with limited miscibility, or even with intermediate compounds.

We can find a possible explanation of the case of FeO by reference to the somewhat analogous oxides of two other metals of the eighth group, namely, platinum and iridium.[6] The evidence indicates that the oxide IrO, within a certain range of temperature, has a higher dissociation pressure than the oxide IrO_2; hence IrO will spontaneously change into a mixture of IrO_2 and metallic iridium, according to the reaction:

$$2IrO = IrO_2 + Ir$$

Thus, if FeO happens, over some particular range of temperature, to have a higher dissociation pressure than Fe_3O_4, it is possible for the following reaction to occur:

$$4FeO = Fe_3O_4 + Fe$$

The existence of such a relation would explain many of the experimental results already obtained, such as the fact that, in

[5] HILPERT, S., and BEYER, J. Ber. deu. chem. Ges., **44**: 1608–1619. 1911.

[6] WÖHLER and WITZMANN. Zs. Elektrochem., **14**: 97–107. 1908. WÖHLER and FREY. Ibid., **15**: 129–142. 1909. A solid solution of IrO_2 with IrO or Ir forms, rather than the pure oxide IrO_2.

our experience, powdered iron heated in oxygen at low pressures always yields a mixture of a black magnetic oxide (perhaps a solution of FeO in Fe_3O_4) and metallic iron. The facts are so few, however, that this explanation is not to be considered as more than a suggestion.

There is one interesting geological application of this relation, if it should be found to exist. Many basic rocks, such as diabase and gabbro, contain metallic iron. The best known occurrence is probably that in Greenland, but other examples exist in all parts of the world. If our supposed oxygen-pressure relationship still holds when the oxides are dissolved in a silicate magma, the following reaction would occur:

$$4FeSiO_3 \text{ (in complex silicate)} \rightleftarrows Fe_3O_4 + Fe + SiO_2 \text{ (in complex silicate)}$$

At constant temperature, increasing pressure would drive this reaction in the direction of diminishing volume. The formation of FeO from Fe and Fe_3O_4 is accompanied by a contraction of volume, according to Hilpert's data, and it appears not unlikely, therefore, that release of pressure in a rising column of molten diabase might alone account for the occurrence of metallic iron in the resulting rock, without the need of recourse to reducing agents such as entrapped organic deposits or dissolved reducing gases. This problem calls for the measurement of dissociation pressures and specific volumes of the oxides and silicates concerned, in the region 900°–1300°.

The same reaction might conceivably be made a basis for a commercial method of making pure iron, free from the usual impurities which come from the use of coke as a reducing agent.

Continuing our survey in the direction of increasing content of oxygen, we come to the compound ferrosoferric oxide, magnetite (Fe_3O_4). Its melting point is 1580°, and it melts sharply to a mobile liquid which crystallizes in octahedra on cooling. Its dissociation pressure is extremely low, being less than 0.04 mm. of mercury at 1200°, and less than 0.005 mm. at 1100°.

Further addition of oxygen brings us into the region between Fe_3O_4 and Fe_2O_3, a region which we have recently investigated

at 1100° and 1200°. These two oxides seem to form a continuous series of solid solutions from Fe_2O_3 to Fe_3O_4, or at least to a point so near Fe_3O_4 that it has not been possible to detect a break in the dissociation pressure curves.[7]

The melting temperatures (solidus and liquidus curves) of the series Fe_2O_3–Fe_3O_4 have not yet been determined. The dissociation pressure rises so rapidly with increase of temperature that at the melting temperature of the solid solution the pressure of oxygen will probably be found to be of the order of several atmospheres for compositions which depart much from Fe_3O_4.

The melting point of Fe_2O_3 can be determined only under sufficient oxygen pressure to prevent its dissociation, and it is impossible to predict whether the melting point will be higher or lower than that of magnetite. The form of the liquidus and solidus curves (continuous, minimum, or maximum) can also not be predicted. The form of these curves is of particular interest in connection with the effect of changing oxygen pressure. At a given temperature it is possible that increasing the oxygen pressure might cause either fusion or solidification of the oxide, or even fusion followed by solidification, depending upon the form of the curves.

The type of solid solution represented by these two oxides of iron deserves a moment's consideration. The special feature of this case is that the two constituents of the solution differ only in the proportion of volatile component which is combined with the non-volatile component. In other words one of the constituent oxides of the solid solution is produced by direct dissociation of oxygen from the other oxide. The case of Fe_2O_3–Fe_3O_4 is thus exactly analogous to the case of $CoCl_2.6NH_3$–$CoCl_2.2NH_3$, in that we may consider Fe as replaced by $CoCl_2$ and O by NH_3. The system just referred to has been studied by Biltz and Fetkenheuer,[8] who find a continuous series of solid solutions, throughout which the NH_3 pressure falls continuously, following a reversed curve of the same form as that shown by the iron oxides.

[7] Sosman and Hostetter. Jour. Am. Chem. Soc., **38**: 807–833. 1916.
[8] Biltz and Fetkenheuer. Zs. anorg. Chem., **89**: 106. 1914.

Several interesting problems are raised by the consideration of this type of solid solution. In the first place how are we to picture to ourselves its internal structure? The X-ray analysis of crystal structure is so radically altering our conceptions of the make-up of solid substances that our ideas of solid solutions have not yet become adjusted to the new facts. When it was discovered that certain properties of a solute in dilute aqueous solution made the solute seem quite analogous to a gas, and when it was discovered that solid solutions existed which seemed quite analogous to liquid solutions, we felt secure for a time in this extension of molecular theory from gases over into liquids and solids. The facts now need re-interpreting, but the greatest need is for more facts on the crystalline structure of solid solutions.

Another problem raised by a consideration of the hematite-magnetite series is that of the continuous transition from one crystal class into another. According to the original conception of isomorphism, two compounds could enter into solid solution only if they crystallized in the same system. Now hematite is hexagonal while magnetite is isometric; is a continuous series from one of these systems to the other possible? To say that there is a hexagonal form of magnetite, which is the form that dissolves in hematite, is merely to dodge the issue; such a statement becomes a meaningless form of words if the experimental consequences remain the same whether the supposed second form exists or not.

A consideration of the point systems from which the crystal classes can be made up shows that we can in reality get a continuous transition from cubic to hexagonal. Suppose a cubical portion of some cubic lattice to be standing on one of its corners; then if it be compressed along the vertical diagonal axis it changes into a rhombohedron which becomes flatter with increasing compression, and the rhombohedron is a hexagonal form. This transition requires of course that the lattice of the isometric and hexagonal forms be thus transformable, and this can be determined for hematite and magnetite only by X-ray studies of their crystals. If it should then be proved that the struc-

tures of the ordinary forms of hematite and magnetite are not thus transformable, then by geometry alone, without the aid of chemistry, could we predict that there must be a break in the solid-solution series between these two oxides?

A third problem of the hematite-magnetite series concerns the escaping tendency or fugacity of the oxygen which dissociates from the oxide. What determines the equilibrium pressure of this oxygen for a given composition of the solid solution? It is interesting to note the peculiar form of the oxygen pressure curve in this series. The middle portion is fairly flat, and the pressure changes slowly with change of composition. As the composition of magnetite is approached, however, the pressure begins to fall rapidly, and, conversely, it rises rapidly as the composition Fe_2O_3 is approached. We have been able to show[9] that the dissociation pressure of the first small portion of oxygen from pure Fe_2O_3 at 1200° is of the order of magnitude of an atmosphere of oxygen, although the pressure rapidly falls to a few millimeters as dissociation progresses.

From a theoretical standpoint there are two ways of looking upon this form of dissociation curve. On the one hand, we may consider that the curve is asymptotic to the axis of ordinates; in other words, the initial composition of the crystal corresponds exactly to the formula Fe_2O_3, and the dissociation pressure of the first few atoms of oxygen is very high. These atoms come from all parts of the crystal, and their removal brings into play forces which greatly restrain the fugacity of all the remaining oxygen atoms, causing a rapid fall in the dissociation pressure.

On the other hand, we may consider, as Langmuir[10] and others have shown, that there are free chemical forces at the surface of the crystal, and that these forces hold atoms of oxygen "adsorbed" on the surface when the crystal is exposed to air. The initial composition then is Fe_2O_{3+x}, in which x is a very small number. The fugacity of these surface atoms is high, but not much higher than that of oxygen atoms just within the surface. Oxygen will begin dissociating from interior parts of the crystal,

[9] HOSTETTER and SOSMAN. Jour. Am Chem. Soc., **38**: 1188–1198. 1916.
[10] LANGMUIR, I. Jour. Am. Chem. Soc., **38**: 2221–2295. 1916.

therefore, before all the adsorbed oxygen is removed from the surface. Mathematically speaking, we may say that the dissociation pressure curve is not asymptotic to the axis of ordinates, drawn at the composition Fe_2O_3, but crosses this axis at a small angle. This second conception of the case gives, I believe, the better interpretation of the facts.

MAGNETIC PROPERTIES AND POLYMORPHISM OF THE OXIDES

The problems so far considered are all problems which are common to nearly all the chemical elements and their compounds. But there is one field of physics in which iron holds at present the first place in interest, namely, the field of magnetism. Progress in the experimental study of magnetic properties has lagged behind experimental progress in electricity, chiefly because we possess no magnetic insulator. As has been well stated by Mr. Sanford at a recent meeting of the Philosophical Society of Washington, "Measuring magnetic properties is like measuring electrical resistance with the Wheatstone bridge and all the connections immersed in a conducting liquid." Nevertheless, rapid progress is now being made on several lines of magnetic research.

The oxides of iron have been, from this standpoint, rather neglected. Measurements will be found here and there in connection with studies of the salts of iron, crystalline or dissolved. From these it is clear that the oxides are not to be classed magnetically with the majority of the iron compounds. Ferric oxide is abnormally low in susceptibility, in comparison with the common salts of iron. Ferrosoferric oxide, on the other hand, belongs, as is well known, among the highly ferromagnetic substances. Ferrous oxide, again, seems to be in a class with ferric oxide. Intermediate oxides possessing a variety of combinations of magnetic properties also exist.

The inversions in ferric oxide first attract our attention. Honda[11] has found that at liquid air temperatures ferric oxide has only about two-thirds as great a susceptibility as at room temperature, and that a change occurs rather suddenly in the

[11] HONDA, K., and SONÉ, T. Sci. Rep. Tohoku (Sendai), **3**: 223–234. 1914.

neighborhood of −40°. The susceptibility rises to a maximum at about 600°, and then falls rapidly to about half value at 690°, where the curve changes direction practically by a right angle, the susceptibility being nearly constant from 690° to 1300°.

We have confirmed the high temperature inversion, placing it at 678° by means of thermal curves.[12] The inversion is sharp and reproducible, and appears on both rising and falling temperature curves. The −40° inversion we have not yet investigated thermally.

Curie[13] discovered a similar magnetic inversion in magnetite at about 535°. Barton and Williams[14] confirmed this inversion, placing it about 545°. Weiss and Foex[15] placed the inversion at 581°, Wologdine[16] at 525°. The temperature of the magnetic inversion is undoubtedly influenced by the magnitude of the induction or of the magnetizing force. No thermal study of the inversion has yet been made. The principal precaution to be observed is the avoidance of oxidation of the magnetite by air. Some of the conclusions of Weiss and Foex seem to have been vitiated by a slight oxidation of their artificial magnetite, and a faint trace of the 678° point of Fe_2O_3 appears on their magnetite curve.

The magnetic inversion in pure iron occurs at about 770°, varying somewhat with the magnetizing force to which the iron is subjected. It is found thermally at 768°, and by electrical resistance, at 757°. This is the thermal inversion known as A2, whose existence in pure iron free from carbon was seriously questioned some years ago, but which has been established as an independent and characteristic inversion by the excellent work of Burgess and his co-workers at the Bureau of Standards.[17]

These magnetic inversions, which occur not only in iron, magnetite, and hematite, but also in various ferrites, are all very

[12] Sosman and Hostetter. Jour. Am. Chem. Soc., **38**: 831. 1916.

[13] Curie, P. Ann. chim. phys., **5**: 322. 1895.

[14] Barton, E. H., and Williams, W. British Assoc. Rep., pp. 657–658. 1892.

[15] Weiss, P., and Foex, G. Arch. sci. phys. (Genève), **31**: 5–19, 89–117. 1911.

[16] Compt. rend., **148**: 776. 1909.

[17] Burgess and Crowe. Bull. Bur. Std., **10**: 315–370. 1914. Burgess and Kellberg. Ibid., **11**: 457–470. 1914.

similar in the form of their temperature-magnetism curves. In each case the effect of rising temperature appears some distance below the inversion point, and increases more and more rapidly as the inversion is approached. One cannot avoid the conclusion that these inversions all have the same fundamental basis. When that basis is found, we will have considerably advanced our knowledge both of polymorphism and of magnetism.

So much has been said about polymorphism (including under this term allotropy, polymerism, and all the other names given to the phenomena of sudden change of physical and chemical properties without change of percentage composition), and so much that has been said is mere quibbling over the meanings of words and phrases, that I shall not undertake any general review of the questions that are raised by the inversions of iron and its oxides. But there is one problem to which considerable attention has lately been given, namely, the problem of the two types of polymorphism in crystalline substances.

Polymorphic changes in crystalline solids can be divided roughly, as is well known, into two groups. On the one hand, there are those changes which carry with them rather profound changes in physical and chemical properties and which often require considerable time to bring about. On the other hand are those reversible changes which occur without delay at a given temperature and which involve relatively small changes in crystal form and in physical properties. An excellent example of a substance showing both types distinctly is silica. SiO_2 occurs in three principal forms, quartz, tridymite, and cristobalite, which are only slowly transformed one into another, and which have certain ranges of stability outside of which they frequently occur in an unstable but very persistent state.* Each of these principal forms, on the other hand, possesses one or two inversion points, at which reversible crystalline changes occur: quartz at 575°; tridymite at 117° and 163°; cristobalite at a temperature varying from 200° to 275°, depending upon the previous history of the crystal.[18]

[18] FENNER, C. N. Am. Jour. Sci., **36**: 331–384. 1913.

Two different views have been held concerning the relation of these two classes of polymorphic inversion, although in our present ignorance of atomic structure neither can be very precisely stated. It has been supposed, on the one hand, that the slow changes were the fundamental ones, involving a rearrangement of the atoms in the molecule or a change in the molecular weight, the expression "molecular weight" being considered to have a meaning in the solid as in the gaseous state. The rapid reversible inversions, then, were held to be merely rearrangements among the molecules, involving slight changes in the crystalline form or symmetry.

But on the other hand we may consider the rapid reversible inversions as the fundamental ones, possibly occurring even within the atomic nucleus itself, and thereby necessarily producing some corresponding change in the spacing of the atoms. The slow and sometimes irreversible changes would then be the less fundamental, involving only a re-grouping of atoms or atom complexes.

The second of these two views seems to me to be supported by the phenomena of polymorphism of the oxides of iron. It is obvious that the change can not be one that occurs in the iron atom independently of its chemical environment, for the magnetic inversion occurs at different temperatures in the different oxides and carbides. Furthermore, corresponding inversions are yet to be found in various other compounds of iron. But there is one oxide of iron which I have not yet touched upon, whose properties shed considerable additional light on the problem. I refer to the magnetic ferric oxide which was discovered by Robbins[19] in 1859, was almost forgotten until recently studied by Hilpert,[20] and on which we are now engaged in further experiments.

[19] ROBBINS, J. Chem. News, **1**: 11–12. 1859. Its discovery has usually been ascribed to MALAGUTI, F. Compt. rend., **55**: 350–352. 1862.

[20] HILPERT, S. Ber. deu. phys. Ges., **11**: 293–299. 1909. Hilpert's rather disappointing conclusion from his excellent experiments is that "Fe_2O_3 functioning as an acid is the carrier of magnetism." But what is "Fe_2O_3 functioning as an acid" in a compound whose total composition is expressed by the formula Fe_2O_3? Furthermore, as Hilpert himself recognizes, not all "ferrites," in which Fe_2O_3 is assumed to be the acidic oxide, are ferromagnetic.

If precipitated magnetite is oxidized by ammonium persulfate, or even by atmospheric air at a low temperature, the product, although it contains almost no ferrous iron and is reddish brown in color, is practically as magnetic as magnetite itself. If this magnetic oxide is heated to 750° for a few minutes, its highly magnetic character is lost, and it becomes like ordinary ferric oxide. What is still more remarkable is that the magnetic Fe_2O_3 has a Curie inversion just above 500°, similar to that of magnetite.

Here, then, we have as fundamental a chemical change as it is possible to get—no mere polymerism, but a change in the formula weight with a reduction of the ferrous iron content from $33\frac{1}{3}$ per cent to zero; yet the magnetic susceptibility and inversion point remain the same. Except for the color, it is as if we had merely ground up the magnetite and mixed it with powdered solid oxygen.

A consideration of the preceding facts concerning the inversions of iron and its compounds, and especially of the interesting properties of the magnetic form of Fe_2O_3, suggest that the magnetic properties and the inversions of iron and its compounds are bound up with the *spacing and arrangement of the iron atoms*, almost without regard to the other atoms present.[21]

What is this structure of the iron atoms which produces the high permeability, and what is the nature of the intra-atomic change at the inversion point?

These problems are on the way to a solution, for Hull has recently found by means of X-ray spectra that the lattice of metallic iron is the centered cube.[22] He discovered also that this structure seems to remain unchanged through both the

[21] This has been suggested for the Heusler alloys: TAKE. Faraday Soc. Trans., 8: 177. 1912. Professor PUPIN, speaking in the recent symposium on the structure of matter, at the American Association meeting in New York, December 27, 1916, stated that he had come to the conclusion from the magnetic properties of very pure iron that its magnetism is intimately related to its crystalline structure. On the other hand, as Hilpert points out, precipitated oxides that are apparently amorphous and that pass readily into colloidal solution can be made, which are magnetic and possess magnetic inversions. Have the particles of these colloids a microcrystalline structure, as yet unrecognized?

[22] Paper presented at the Cleveland meeting of the American Physical Society, November, 1916.

A2 and the A3 inversions, further confirming the view expressed above, that these inversions are intra-atomic. Further light could be obtained on the problem by a comparison of the structures of the magnetic and the non-magnetic forms of Fe_2O_3.

This apparent dependence of magnetic properties upon the arrangement of the iron atoms in space opens up interesting possibilities. If magnetite can be oxidized to ferric oxide without loss of its magnetism, it may be possible to convert it into other compounds, or even to convert metallic iron into compounds of iron, in which the arrangement of iron atoms will remain undisturbed. A highly magnetic compound of iron with a high electrical resistance, for example, might possess industrial as well as academic interest.

Having barely touched upon some of the problems in chemistry and physics that are raised or partially solved by the study of the oxides of iron, I wish to devote the little time that remains at my disposal to the consideration of a few of the geological problems connected with these oxides.

THE OXIDES OF IRON AS RELATED TO CERTAIN GEOLOGICAL PROBLEMS

The oxides of iron rank high among the earth's important minerals, since metallic iron is manufactured almost exclusively from oxide ores.[23] Questions of genesis of the ores of iron therefore furnish topics of perennial interest to the economic geologist. The widespread occurrence of these ores makes them also of interest to the student of historical and structural geology.

At the present time the so-called magmatic and pneumatolytic ores are attracting the most attention from a scientific standpoint, though economically they are secondary in importance to the sedimentary and residual ores. The magmatic-pneumatolytic ores range in composition all the way from magnetite to hematite. Two different modes of origin account for them. Certain large magnetite deposits are claimed to have been deposited in the lower portion of large igneous masses by gravitative settling of magnetite crystals while the mass was still molten. This

[23] Carbonate ore formed only 0.006 per cent of the production in the United States in 1915. (E. F. Burchard.)

is the explanation offered for many of the deposits of titaniferous magnetite, such as the Ramsoy deposits of Norway.[24] It has also been suggested that the magnetite may have separated by gravity as a liquid or partly liquid layer while the entire magma was still molten.[25] These explanations based on magmatic differentiation have met with various difficulties, geological as well as chemical and physical. The separation of a liquid layer of pure magnetite, for instance, is hardly believable, since the melting point of magnetite is 1580°, whereas the intruding rock bodies from which it separated could hardly have been at a temperature of more than 1000°. Whether small quantities of other substances might greatly lower the melting temperature of magnetite is one of the problems yet to be solved experimentally.

The other mode of origin assumes that the iron was carried in the hot solution or vapor given off by an intruding igneous mass. There are many deposits for which this mode of origin seems well established. Examples of these are the magnetite deposits of Cornwall, Pennsylvania,[26] and the hematite-magnetite ores of the Island of Elba.[27]

An interesting feature of the latter, which we discovered in the course of some magnetic measurements, is the zonal development of certain crystals.[28] The hematite crystals from Elba are well known for their large size and excellent development. They are not pure Fe_2O_3, however, but contain a considerable percentage of ferrous iron. By chemical analysis and by magnetic measurements we have shown that the ferrous iron is zonally distributed, being higher in the core and base of the crystal and lower in its outer surface and free-growing tip. Evidently, the temperature or oxygen concentration, or both, were changing continuously in one direction while these crystals were being deposited.

The reactions that will lead to the deposition of hematite, hematite-magnetite, or pure magnetite from a vapor or a liquid

[24] FOSLIE, S. Norges Geol. Unders., vol. 4, 1914.

[25] DALY, R. A. *Origin of the iron ores at Kiruna.* Vetensk. prakt. Unders. Lappland. Geology, No. 5. 1915.

[26] SPENCER, A. C. U. S. Geol. Survey, Bull. 359. 1908.

[27] LOTTI, B. Mem. descr. carta geol. Italia, II. 1886.

[28] Jour. Wash. Acad. Sci., 6: 309. 1916.

solution are yet to be investigated. It is not certain, even, what compounds of iron were originally present. The natural suspicion is that the iron was present as chlorides or fluorides, since these compounds are known to be volatile at comparatively low temperatures. Many geologists have objected that in some cases the associated rocks show no trace of alteration by pneumatolytic action, or contain little or none of the element supposed to have been combined with the iron. The Kiruna magnetite ore-body of Sweden, for instance, shows sharp contacts against unaltered normal prophyries. But in the face of a phenomenon such as that seen at Kilauea, where vast quantities of sulfur and its compounds are given off from the lava lake, leaving hardly a trace of sulfide of any kind in the solidified lava around the crater, we need not feel discouraged about proceeding with experiments on the deposition of iron oxides from those compounds which are readily volatile and on which the basic data of temperature and concentration, at least, are obtainable.

One set of facts regarding hematite deposits of the magmatic-pneumatolytic type is to be noted at this point, namely, their magnetic properties and their content of ferrous iron. We have found by some preliminary, as yet unpublished, measurements that the force exerted upon a solid solution of Fe_3O_4 in Fe_2O_3 by a non-uniform magnetic field is roughly proportional to the percentage of FeO. This holds true for both artificial and natural oxides, including even some martites high in ferrous iron. On the other hand, oxides containing ferrous iron (perhaps as carbonate or as other compounds), but in which the FeO is not in solid solution, such as the limonite from Mt. Ktaadn, Maine, have a much lower susceptibility than the corresponding solid solution.

Again, an oxide formed by the oxidation of precipitated magnetite, as has been mentioned above, may have a very high susceptibility, although the percentage of FeO may be very small. We have examined one such oxide found by Messrs. Graton and Butler in a gossan deposit. Hilpert reports that examples have been found in Europe in association with carbonate ores which

are undergoing oxidation. The usual "magnetic hematite," however, owes its magnetic properties to its ferrous iron content.

A simple magnetic test, then, combined with a determination of the ferrous iron, permits certain preliminary conclusions as to the origin of many natural oxides of iron. But there are other magnetic properties which we have not yet touched upon, which may be expected to vary with the composition and constitution of the oxide, such as the remanence and the coercive force, and especially the variation of the magnetic properties with temperature. This correlation of magnetic, physical, and chemical properties is not a small task, but it is one for which the apparatus and methods are now in good working order.

The remanence, or permanent magnetization, offers particular interest. It is well known that magnetite crystals are frequently found which are very strong permanent magnets; in fact the history of magnetism dates from the discovery of these "lodestones" by the ancients. Yet most natural magnetite is not polarized. What causes have produced the polarization and how are they related to the origin and history of the ore?

There is time to touch only in the briefest way on the problems connected with other types of iron ores. The study of replacement ores leads us into the still obscure problem of replacement as a geological phenomenon, ably discussed by Lindgren in a recent paper[29] but still, unfortunately, the subject of more discussion than experiment. The secondary concentration of oxide ores by circulating waters is another problem in chemistry at ordinary temperatures which has not yet received the attention it deserves.

Even the origin of ores which are admittedly almost unaltered is still somewhat obscure. The genesis of residual ores such as those of Cuba is not so much a problem of the oxides of iron, since these play rather a passive role, as of the weathering of iron-bearing silicates. But the origin of certain sedimentary deposits is a specific problem in the chemistry of iron, complicated, however, by a new factor, the biological. It has long been known that some of the higher bacteria play a part in the pre-

[29] LINDGREN, W. *The nature of replacement.* Econ. Geol., **7**: 521–535. 1912.

cipitation of hydrated ferric oxide, and the number of forms which are known to be associated in some way with the precipitation is constantly increasing. It is not yet clear in all cases whether the organism actually brings about the reaction through its own life processes, whether the precipitation is due to the decomposition of the dead organism, or whether the organism acts merely as a nucleus for the collection of agglomerating colloidal oxide. The origin of the immense and very pure iron ores of Minas Geraes, Brazil, is ascribed by Harder and Chamberlin[30] to bacterial activity, apparently for the indirect reason that there are objections to any other mode of formation. The reader is left with the uneasy feeling that perhaps only our lack of knowledge prevents our objecting to the bacterial explanation as well.

There is one possibility which deserves attention in this connection. Experiments with closed tubes show that a comparatively moderate increase of temperature will hydrolyze various ferric salt solutions, and precipitate ferric oxide, which does not redissolve. These ferric solutions seem relatively unstable and easily hydrolyzed, and the colloidal ferric oxide only needs to be agglomerated to form a precipitate that will settle. Are there any possible variations in the composition, concentration, or temperature of sea water which would cause it to precipitate the ferric oxide from a hydrolyzed, even very dilute, ferric solution in much the same way as the Mississippi silt is precipitated by the waters of the Gulf of Mexico? Bacteria, able and willing to take advantage of the conditions favorable to the reaction, need not be excluded, but, as may be the case with calcium carbonate,[31] inorganic causes may be primarily responsible.

The intimate association of silica with many ores, amounting even to chemical combination, as in some of the siliceous ores of the Lake Superior region, may represent a simultaneous agglomeration of colloidal silica and ferric oxide, or an adsorption of ferrous and ferric iron by agglomerated silica. It is to be noted, also, that such precipitated colloids can sometimes be

[30] Jour. Geol., **23**: 385–404. 1915.

[31] See JOHNSTON and WILLIAMSON. Jour. Geol., **24**: 729–750. 1916.

re-dispersed (peptonized) by pure water, simply through the leaching out of the salts carried down by them from the strong precipitating solution. A method of secondary concentration is thereby suggested. It is evident that from studies in colloid chemistry we may expect considerable advances in our knowledge of the sedimentary ores.

I have presented a rather varied list of problems, some of which may seem remote from pure chemistry, but I may possibly find an excuse in the fact that this meeting has been held as a joint meeting of the Chemical Society and the Washington Academy of Sciences. As soon as we begin to consider them in detail, we find that the problems of the oxides of iron are but phases of some of the greater problems of chemistry, physics, biology, and geology. And they can not be solved by taking thought about them; new facts, to be yielded by new experiments and new observations, are demanded. Nor are the problems as simple as some of them may have appeared from my statement of them. The chemist is amazed by the facile transformations of iron from ferrous to ferric, beholding the two states of oxidation acting like two absolutely different elements. The physicist stands appalled before the spectrum of iron, realizing the many unknown quantities hidden behind its thousands upon thousands of lines. Even the layman can get a vivid realization of the complexity of the problems involved; he has but to walk out through the country round about Washington and note the bewildering play of inorganic colors everywhere about him, ranging from deep brown-black through various shades of drab, brown, purple, and maroon, and through the many tints of pink, ocher, and rose, to the most brilliant of reds and orange-yellows, and then realize that almost every one of these hundreds of colors is due to an oxide or hydrated oxide of iron; he will begin to realize then that our chemical knowledge of these oxides is almost infinitesimal. One thing only is clear to us, and that is that we are only skirting around the edges of that vast body of knowledge about iron and its oxides which is, as the mining geologist says, "in sight," not to mention the unsuspected problems that lie "in depth," far beyond our farthest plans for research.

GEOLOGY.—*Note on the diffusion of sodium chloride in Appalachian oil-field waters.*[1] G. B. RICHARDSON, Geological Survey.

During the summer of 1915, while working in the oil fields of Butler County, Pennsylvania, I became interested in the common occurrence of brines in oil wells. Samples of salt water were collected and an analysis (A) of one was made in the Geological Survey laboratory. This analysis is compared with another analysis (B) of deep-seated water from Washington County, Pennsylvania, made by Steiger (see table 1). The wells from

TABLE 1

ANALYSES OF WATER FROM DEEP WELLS IN WESTERN PENNSYLVANIA

	COMPOSITION OF DISSOLVED SALTS	
	A	B
Cl	62.29	61.38
SO_4	0.10	0.02
HCO_3	None	....
CO_3	None	None
Br, I	....	0.26
Na	27.59	24.50
K	0.10	1.97
Li	Trace	....
Ca	8.40	9.56
Mg	1.47	0.94
Sr	Trace	1.31
Ba	Trace	Trace
Fe''	0.05	0.06
Fe'''	Trace	....
	100.00	100.00
Concentration, parts per million	131,890	263,640

A. Water from "hundred-foot sand" at depth of 1359 feet, in well on farm of Charles Hoffman, 5 miles northeast of Butler, Pennsylvania. Analysis by W. B. Hicks and R. K. Bailey, U. S. Geological Survey.

B. Water from Oriskany sandstone at depth of "6300" (6260?) feet, in well of Peoples Natural Gas Company, 5 miles northwest of McDonald, Pennsylvania. Analysis by George Steiger, U. S. Geological Survey. See U. S. Geol. Survey Water-Supply Paper 364, p. 9, 1914.

[1] Published by permission of the Director, U. S. Geological Survey.

which the samples were taken are about 40 miles apart, and the water-bearing horizons, of Devonian age, are separated stratigraphically about 4500 feet.

The history of deep-seated waters of this kind is a subject of debate. In a recent number of *Economic Geology* I have suggested, as a working hypothesis, that the Appalachian oil-field brines are a mixture of waters originally occluded with the sediments when deposited and of meteoric waters of later origin which have entered the rocks during periods when the region was above sea level; that these waters have leached great masses of sedimentary beds containing disseminated salt, and that they have undergone a series of changes in composition, the saline matter tending to accumulate because of the slow circulation dependent on the synclinal structure of the region. Among other causes of the sodium chloride content of the waters and of the increase of concentration with depth, I suggest that diffusion from beds of rock salt may be an important factor. Such beds in the Salina formation are known to underlie at least part of the Appalachian oil-fields. Thick deposits of rock salt actually occur 600 feet below the horizon in the well from which the water of sample B was obtained, and others may occur.

It is worthy of consideration that beds of shale, especially connecting lenses of sandy shale, separating the more porous beds of sandstone in the Appalachian oil-field section may be porous to such an extent that there exists a continuous, though very irregular, network of minute pore spaces connecting the beds of rock salt with the overlying beds in which salt water is found. The deep-seated waters are under great artesian pressure, as shown by the fact that in the well from which the sample represented by analysis B was obtained the water was forced 4000 feet above the horizon where it was encountered in drilling. Such pressure tends to fill with water the pores even of very fine-grained strata, and it seems plausible that in the rocks of the Appalachian oil-fields there are continuous pore spaces occupied by water. If such conditions exist, diffusion must act.

Table 2, based on a paper by Becker[2], was kindly prepared for me by C. E. Van Orstrand.

TABLE 2

MIGRATION OF SODIUM CHLORIDE IN PURE WATER

DISTANCE	TIME	CONCENTRATION
meters	*years*	
000	1,000,000	1.00
500	1,000,000	0.06
1000	1,000,000	0.0002
1500	1,000,000	0.00000003
000	10,000,000	1.00
500	10,000,000	0.56
1000	10,000,000	0.24
1500	10,000,000	0.08
000	20,000,000	1.00
500	20,000,000	0.68
1000	20,000,000	0.41
1500	20,000,000	0.21

The concentrations are expressed in terms of the initial concentration at the plane of contact between a bed of salt and the base of a column of initially pure water. It is assumed that the initial concentration remains constant.

The computed concentrations are of course only suggestive, and the figures can not be directly applied to the Appalachian region because initially pure water was assumed in computing the table, whereas the water through which diffusion may have occurred must have been initially saline. Nevertheless, the table is of interest in an attempt to account for the high concentration of the brine represented by analysis B and for the general increase in concentration of Appalachian oil-field brines with depth.

[2] BECKER, G. F. *Note on computing diffusion.* Am. Jour. Sci., **3**: 220–226. 1897.

ABSTRACTS

Authors of scientific papers are requested to see that abstracts, preferably prepared and signed by themselves, are forwarded promptly to the editors. Each of the scientific bureaus in Washington has a representative authorized to forward such material to this journal and abstracts of official publications should be transmitted through the representative of the bureau in which they originate. The abstracts should conform in length and general style to those appearing in this issue.

GEOLOGY.—*The Gold Log mine, Talladega County, Alabama.* E. S. BASTIN. U. S. Geological Survey Bulletin 640-I. Pp. 159–161. 1916.

The geologic features of a gold mine that has been worked intermittently for seventy years near Talladega, Alabama, are described. The country rock is Talladega slate, probably of Lower Cambrian age. The ore consists of (1) irregularly interlocking white to light-gray quartz, white to pale-pink calcite, and very minor amounts of sulphides and free gold, and (2) schist partly replaced by some or all of these minerals. Chalcopyrite is the principal sulphide. Free gold occurs locally in irregular masses in the quartz.

The value of the gold and silver recovered is reported to average about $4 to the ton of ore treated. R. W. S.

GEOLOGY.—*Ozokerite in central Utah.* HEATH M. ROBINSON. U. S. Geological Survey Bulletin 641-A. Pp. 1–16, with 1 plate. 1916.

The American needs for ozokerite (a substance commonly known as mineral wax) have been largely met in the past by imports from the Galician mines in Austria, but interest in the domestic supply has recently been stimulated. The largest district in the United States in which it has been mined and prospected is an area in central Utah a little more than 12 miles long and from 1 to 4 miles wide between Gilluly and Colton.

The rocks of this field have a total thickness of about 4000 feet and were deposited as nonmarine sediments in early Tertiary (Eocene) time. The lower 1000 feet of the beds exposed are known to contain ozokerite, and the remaining 3000 feet contain bituminous or oil shale

interbedded with other rocks. The principal ozokerite mines and prospects have been opened in the Wasatch formation and are scattered irregularly through a stratigraphic distance of 600 to 700 feet. The ozokerite fills cavities that have resulted from fracturing. The composition, properties, origin, and uses of ozokerite are discussed, and the mines and prospects are described. R. W. S.

GEOLOGY.—*The oil and gas geology of the Foraker quadrangle, Osage County, Oklahoma.* K. C. HEALD. U. S. Geological Survey Bulletin 641-B. Pp. i–iv, 17–47, with 2 plates and 11 figures. 1916.

This paper describes and portrays those features of the Foraker quadrangle that may be of interest and assistance in the discovery and development of accumulations of oil and gas. Under the heading "Stratigraphy" those strata valuable as key horizons in mapping structure are described in detail, and the probable positions of oil sands are given. The geologic structure is portrayed by map and stereogram, and the anticlines believed to be favorable for the accumulation of oil and gas are described in detail. In conclusion specific recommendations for prospecting are given, and the writer's belief concerning the probability of the occurrence of oil and gas accumulations is set forth. R. W. S.

GEOLOGY.—*Possibilities of oil and gas in north-central Montana.* EUGENE STEBINGER. U. S. Geological Survey Bulletin 641-C. Pp. 49–91, with 4 plates. 1916.

The thick bodies of Upper Cretaceous shale with which most of the oil and gas in both Wyoming and Alberta are associated are known to be continuous between these two localities under the plains of Montana, making it apparent that favorable structural features, especially anticlines and domes similar to those that are productive in Wyoming and Alberta, offer a chance of success with the drill in this part of Montana. The facts observed appear to warrant the conclusions that a considerable gas territory, comparable in extent to the Alberta fields, may be found, and that the area shows some probability of yielding oil.

The character and distribution of the sedimentary rocks, particularly those of importance in the search for oil and gas, are discussed, and the geologic structure of north-central Montana is described. Particular attention is paid to the structural features of the area of tilted and faulted rocks north and south of the Bearpaw Mountains. R. W. S.

GEOLOGY.—*Molybdenite and nickel ore in San Diego County, California.* F. C. CALKINS. U. S. Geological Survey Bulletin 640-D. Pp. 73–82. 1916.

Molybdenite has been reported to occur at several places in San Diego County. The deposit near Ramona, which has attracted most attention, was visited in December, 1915. The molybdenite at this locality is unevenly disseminated in an aplite dike which cuts granite, the principal rock of the region. The deposit has not been shown to have commercial value, though further development and prospecting seem to be warranted.

A nickel prospect, the Friday mine, near Julian, was also visited. The nickeliferous deposit, which has been explored to a depth of 200 or 300 feet, lies at an irregular contact between mica schist and gabbro. It consists mainly of pyrrhotite, but contains pyrite, chalcopyrite, and an iron-nickel sulphide, probably polydymite. Both in constitution and mode of occurrence it resembles the Sudbury deposits and is presumably similar in origin. The sulphides are high enough in nickel to constitute ore, provided a fairly large body of them can be uncovered.

F. C. C.

GEOLOGY.—*Gypsum in the southern part of the Bighorn Mountains, Wyoming.* CHARLES T. LUPTON and D. DALE CONDIT. U. S. Geological Survey Bulletin 640-H. Pp. 139–157, with 3 plates. 1916.

Gypsum has been known to occur in a belt of rocks surrounding the Bighorn and Owl Creek mountains, Wyoming, from the early days of exploration. The amount of this material at several places is great, but owing to the slight demand for it little attention has been given to its utilization until the last few years.

The gypsum occurs at two horizons—the upper at or near the top of the Chugwater formation, or Red Beds, and the other in the upper part of the Embar formation. Only the upper bed, however, is of economic importance at Sheep Mountain and in the vicinity of Thermopolis.

The rocks exposed in the region described in this report range in age from pre-Cambrian to Quaternary. The Embar and Chugwater formations, which contain the gypsum beds, are described in detail.

R. W. S.

PROCEEDINGS OF THE ACADEMY AND AFFILIATED SOCIETIES

THE PHILOSOPHICAL SOCIETY OF WASHINGTON

The 781st meeting was held on January 6, 1917, at the Cosmos Club. Vice-President SOSMAN in the chair; 37 persons present. The minutes of the 779th meeting were read in abstract and approved.

Mr. E. BUCKINGHAM gave a paper on *The effect of elastic strain on the equilibrium temperature of a solid and its liquid.* By methods not involving any reference to the details of the theory of elasticity, a general formula was deduced for the effect on the equilibrium temperature of a solid and a liquid under a stress which produces a strain in the solid at the surface of contact with the liquid. No restrictions were imposed on the nature of the body or on that of the strain, except that the strain must be non-dissipative.

The general formula was applied to the case of linear compression, and the result compared with some other formulas which have been proposed. It agrees with Riecke's formula but does not agree with the interpretation sometimes given to Poynting's formula. Comparison with Bridgman's formula did not lead to any definite conclusion.

Mr. E. D. WILLIAMSON gave a second paper on the same subject. The particular case of an isotropic solid under the influence of a one-sided thrust was treated. Formulas were deduced by methods similar to those used by Gibbs for the change of the equilibrium temperature on the face where the thrust was applied, and also at the free surface, on the hypothesis in each case that a reversible equilibrium is possible. At the free surface the change of temperature is always negative and small, i.e. at such a surface the melting point is always lowered by a small amount by any strain whatever. On the other hand at the surface where the stress is applied the effect is very much greater and is negative for a push but positive for a tension. The possibility of the physical realization of this second case is in doubt.

The method can be extended to the case of solubility by the introduction of another variable—namely, the concentration of the solution. The results are similar to those mentioned above, the solubility being very slightly increased over the free surface but increased or decreased on the stressed surface by a push or a tension, respectively, by a much greater amount.

Mr. J. C. HOSTETTER then gave an illustrated communication on *The influence of non-uniform pressure on solubility.* It is possible that fluctuating temperature and, perhaps, some indirect effects brought

about by pressure may account for the solidification of crystals compressed in contact with their solution by loosely fitting pistons—as found by James Thomson, Le Chatelier, and Spring—without the necessity of postulating large increases in solubility due to pressure.

In preliminary experiments, individual crystals were subjected to stress at constant temperature by direct loading, and the effect on the concentration of the surrounding solution studied, by measuring the conductivity. No change in concentration was found. The test was sufficiently sensitive to show that the effect of non-uniform pressure is much less than that produced by the same pressure acting uniformly, and not many times greater, as had been postulated by Johnston and Adams.

However, in another series of experiments in which an unloaded crystal was placed alongside a loaded crystal, the former grew at the expense of the latter, showing that a very slight increase of solubility was produced by the stress. The method of loading the crystals has a large influence on the effects found, thus indicating the importance of the stress distribution.

In conclusion, the experiments of Becker and Day on the linear force of growing crystals were cited as indicating the stability of a crystal in its solution, even when subjected to pressure. In their experiments loaded crystals were found to lift the load during growth, although the pressures on the supporting edges of the crystals were finally of the order of magnitude of the crushing strength of the crystal.

Discussion. The three papers were discussed by Messrs. BRIGGS, BUCKINGHAM, HOSTETTER, SOSMAN, and WILLIAMSON. Mr. Hostetter remarked that the reason for the effect of hydrostatic pressure on melting and solubility was much more obvious than that for the similar effect due to strain in the solid only, as hydrostatic pressure directly aids or opposes the volume changes accompanying such change in state. Mr. BUCKINGHAM referred to the complications introduced by the change in cross section of a crystal under load as it dissolves.

Correction. In the minutes of the 780th meeting, this JOURNAL, **7**: 24. 1917, for "Messrs. Ferner and Rothermel were appointed tellers," read, "Messrs. Fenner and Rothermel were appointed tellers."

D. H. SWEET, *Secretary.*

THE GEOLOGICAL SOCIETY OF WASHINGTON

The 311th meeting was held in the lecture room of the Cosmos Club on November 22, 1916.

INFORMAL COMMUNICATION

T. W. STANTON: *A Cretaceous volcanic ash bed on the Great Plains in North Dakota.* Near Linton, North Dakota, in the southern part of the State about 15 miles east of the Missouri River, there are several conspicuous white outcrops that at a distance suggest chalk or diatomaceous earth. At one of the best exposures, 1 mile southeast of Lin-

ton, the measured thickness of the white bed is 26 feet, and it lies in the Fox Hills sandstone about 35 feet above the top of the Pierre shale. The rock is very fine-grained and mostly massive, though it contains some thin-bedded layers. A sample of it has been examined by Dr. G. F. Loughlin, who finds that it "consists of 80 per cent of volcanic glass, 15 per cent of quartz and feldspar, 2 or 3 per cent of biotite (somewhat bleached) and scattered grains of calcite, hornblende, magnetite, and chlorite."

No fossils were found in the white ash bed itself, but in the sandstone directly overlying it distinctive Fox Hills invertebrates were collected at several horizons distributed through a total thickness of about 100 feet. A fossiliferous green band colored by greenalite, which lies 16 feet above the white bed, also contains a considerable amount of volcanic glass, thus showing that volcanic material is not restricted to the white ash bed.

This seems to be the first recorded observation of such a bed of volcanic ash in the Cretaceous sediments of the Great Plains. The nature and location of the deposit are such that its material must have been carried a long distance in the air and finally deposited in the sea. The nearest probable source, according to present knowledge of Cretaceous volcanism in the Rocky Mountains, is in the Livingston region, Montana, about 500 miles west. Remnants of this great ash shower should occur in other parts of the Great Plains and Rocky Mountains, and when recognized and identified they should be of some service in the definite correlation of local sections.

REGULAR PROGRAM

HENRY M. EAKIN: *The Quaternary history of central Alaska.* Central Alaska is rather evenly divided between uplands that are formed by solid rocks, and a number of basins floored with Quaternary sediments that head far inland and extend, apparently without interruption, to the sea. These basins seem to be interpreted properly as pre-Quaternary erosional depressions. The physical aspects of the region indicate that in Quaternary time the normal drainage outlets of these basins were temporarily dammed, large areas were inundated and silted up, new outlets through low passes in the rims of the old basins were formed, and the drainage of the whole region was reorganized. Various hypotheses as to the nature of the dams have been considered, including crustal warping, lava flows, gravel deposits, and glacier extension across the old basins.

The hypothesis that glaciers were the agents meets the requirements that the dams were formed simultaneously in widely separated localities and were transient. For two major stream diversions and for many minor ones ice damming seems clearly indicated, and no item of positive evidence antagonistic to this hypothesis has been discovered. However, complete knowledge of certain areas essential to the final solution of the problem is still lacking.

J. S. DILLER: *Was the new lava from Lassen Peak viscous at the time of its eruption?* That it was viscous is indicated by the following considerations:

1. The material that rose from the volcanic chimney into the crater on the summit of Lassen Peak spread in all directions and filled the funnel-shaped crater to its rim, forming a lid to the volcano.

2. Upon reaching the crest of the crater's rim the lava overflowed at the lowest points, one stream flowing down the western slope of the peak and another toward Lost Creek on the northeast.

3. The flow down the west slope is about 1000 feet in length and is a normal stream of siliceous lava with very rough broken surface. That it was a hot, viscous mass beneath the surface at the time of its eruption is proved by the written testimony of a number of observers, who from 9.30 to 11.30 on the night of May 19, 1915, watched the glow and flashes of light from the flowing, breaking lava as, in plain view, it crossed the crater rim and descended the slope.

4. In the overflow stream at the head of Lost Creek the delicate, steam-torn lava was bent and folded, as if viscous, while advancing across the crater rim, and much of it was carried away by the tremendous blast of hot gas (from beneath the lid) that devastated the Hat Creek country.

5. When the hot blast escaped from beneath the lava lid a portion of the lid, apparently where hottest, subsided into the former crater and exposed a number of fracture surfaces of lava blocks. On some of these surfaces there are distinct lines of viscous flow, and as the surfaces originated during the subsidence following the great eruption in May, 1915, the lava must have been viscous at that time.

G. W. STOSE: *Age of certain shales in Cumberland-Lebanon Valley, Pennsylvania.* The shales referred to are in detached areas in the limestone valley. The limestones range in age from Lower Cambrian to Ordovician and may be divided into seven formations. The shales were regarded by the Pennsylvania Geological Survey as equivalent to the shales formerly called Hudson River but now called Martinsburg, which overlie the limestones and adjoin them on the northwest. In weathered outcrop the various shales are closely similar and, as east of Harrisburg they have been brought together like parts of the same formation, this miscorrelation is not surprising.

The real age of the shales in the detached areas was determined only after tracing the seven formations of the limestone from their known outcrops in the Carlisle quadrangle, southwest of Harrisburg. The largest area of the shales south of Harrisburg was proved, by its relation to the Elbrook limestone, to be the Waynesboro shale of Middle Cambrian age, and typical purple siliceous shale of the Waynesboro was later found in it. The irregular relations to other formations on its north side are due to overthrust faulting, which terminates the area against the Martinsburg shale east of Harrisburg. The Waynesboro shale occurs also in prominent hills east of Schaefferstown and in small hills near Shillington, southwest of Reading. The shale thins abruptly

toward the east and north and is not visible on the north side of North Mountain, where it is probably present, although thin and covered with wash. Its greater thickness at Schaefferstown and south of Harrisburg is probably due to the fact that at these localities it is overthrust from farther south, where its thickness is greater.

Certain rocks at the Cornwall mines south of Lebanon, Pennsylvania, which were regarded as Hudson River shales by the Pennsylvania Geological Survey, were found to be metamorphosed siliceous banded limestones of the Conococheague limestone of Upper Cambrian age.

T. WAYLAND VAUGHAN: *Significance of reef coral fauna at Carrizo Creek, Imperial County, California.* Owing to the lateness of the hour this paper was postponed to another meeting.

At the 312th meeting, held December 20, 1916, the presidential address was delivered by the retiring President, ARTHUR C. SPENCER: *Stream terraces in the Rocky Mountain province* (Illustrated). The address will be published at a later date.

At the twenty-fourth annual meeting held on the same evening the following officers were elected for the ensuing year: *President*, WALTER C. MENDENHALL; *Vice-Presidents*, FRANK H. KNOWLTON and ARTHUR L. DAY; *Secretaries*, H. E. MERWIN and ESPER S. LARSEN, JR.; *Treasurer*, B. L. JOHNSON; *Members-at-large-of-the-Council*, B. S. BUTLER, H. S. GALE, C. W. GILMORE, R. W. PACK, and L. W. STEPHENSON.

CARROLL H. WEGEMANN, *Secretary.*

THE BOTANICAL SOCIETY OF WASHINGTON

The 116th regular meeting of The Botanical Society of Washington was held in the assembly hall of the Cosmos Club at 8.00 p.m., Tuesday, December 5, 1916, President T. H. KEARNEY presiding.

The program of the evening consisted of a symposium on the behavior of hybrids in different groups of plants.

Mr. G. N. COLLINS discussed the behavior of Indian corn. In about 25 cases out of 50 where the vigor of first-generation hybrids had been compared with that of the parents, definite evidence of greater vigor was secured, and in no instance was there clear evidence of decreased vigor. It was suggested that the differences in the degree of vigor observed in different varietal combinations appeared to be influenced by the length of time the parental strains have been isolated. Strains which are widely separated geographically, and on this account probably have been kept distinct for long periods of time, usually exhibit the greatest increase in vigor when crossed, while strains from the same or adjacent regions, although they may show more marked morphological differences, generally show a less marked increase in vigor in the first generation of the cross.

In a cross between two varieties having many sharply contrasting characters, a comparison of the variability of the first and second gen-

erations showed two characters where the first generation was more variable than the second, six characters in which the second generation was more variable than the first, and eleven characters in which there was no measurable difference. In the same cross, in correlation studies involving eleven contrasted characters with fifty-five possibilities of correlation, twenty cases of correlation were observed. All but five of these correlations, however, appear to be physical or physiological in their nature rather than genetic, such as the correlation between branching space and number of branches.

There are but few alternative or discontinuous characters in maize, and most of these are color differences or differences in chemical composition, as in the endosperm characters.

The discontinuous characters are for the most part Mendelian. Horny or sweet endosperm is perhaps the best example of a simple Mendelian character pair thus far encountered in maize. Horny and waxy endosperm are completely alternative, but there are definite departures from the expected ratios. Aleurone and endosperm color show all gradation between Mendelian monohybrid ratios and continuous inheritance.

Mr. O. F. Cook called attention to differences in behavior of different kinds of plants and animals, as indicating a possibility that the expectation of finding general laws applicable to the whole organic world may not be realized. Each case must be treated in a specific way. Increased vigor in the first generation is one of the more general phenomena attending hybridization. In cotton, for example, when distinct types are crossed, there is usually evidence of increased vigor and hardiness. These are expressed in larger size, better yield, and a greater ability to withstand adverse conditions. By distinct types of cotton are meant types which have a range comparable to the more divergent races of men, or to the Indian zebu as distinguished from our domestic races of cattle. The cotton types appear much more divergent than the types of corn.

The discussion was largely confined to examples in hybridization of cotton. As a rule the conjugate or F_1 generation is intermediate between the parents, while splitting is pronounced in the second and later generations but with no cases of complete return to either ancestral type. As a rule there is a great deal of correlation or coherence in the characters shown in the perjugate (F_2 and subsequent) generations. It has not been possible to secure a cotton combining in stable form the Upland type of vegetation and the Sea Island or Egyptian type of lint. Plants which resemble the Upland type have lint with the Upland characters and vice versa, but the plants that most nearly resemble the parental types in other respects are usually very inferior with respect to abundance and quality of lint.

Thus, one of the results of hybridization may be described as a total loss of the increment of selection which had been developed in the parent stocks previous to crossing. Some characters are more or less discontinuous, but others appear to be continuous. The opportunities for

selection in the conjugate generation are not good, on account of the general uniformity of the plants. Selections have been carried in some cases as far as 12 generations without securing evidences of stable combinations of desirable characters. Hybrids between Sea Island and Upland varieties were not so good as the better class of long-staple Upland varieties, when work with the hybrids was discontinued.

Mr. H. V. HARLAN discussed the behavior of barley hybrids. He first called attention to the strikingly different characteristics of the barley group and the sharply contrasting characters such as naked and hulled grain, black, purple, blue, or white colors, two and six-rowed, awned and hooded heads, smooth and toothed awns, etc. Individuals of the F_1 generation in barley either may be intermediate in character or may resemble one of the parents, and are quite uniform. In most of these crosses the characters are inherited in a 3 : 1 ratio. The substitution of hoods in the place of the awn, which has a very decided effect upon the physiology of the plant, is dominant to the presence of awns. The smoothness or roughness of the awns behaves as a Mendelian character. There is also a correlation between the smoothness of the awn and the hairiness of the stigma. Crossing between the two-rowed and six-rowed barley often results in an intermediate variety. Such characters as the following: hulled and naked, black and white, hooded and awned, are inherited in the 1:3 ratio. Fertility does not necessarily follow the 1:3 ratio.

Dr. C. E. LEIGHTY discussed hybridization in wheat varieties and species. Nine groups are available for hybridization: *Triticum monococcum*, *Triticum polonicum*, wild wheat of Palestine, and six subspecies of *Triticum sativum*. All of these species and subspecies hybridize and fertile hybrids have been obtained, rarely, however, between *Triticum monococcum* and any other group. Wheat and rye hybrids have been secured always by using wheat as the female parent. *Aegilops ovata* and *triticoides* have also been used in hybridization with wheat. The first generation shows increased vigor, so far as noted, and great uniformity. Most of the characters, however, are intermediate. When wild wheat is used in hybridization the spikelets of the hybrid fall apart as does the wild wheat. In the second generation segregation of most characters occurs in a 3:1 or 1:2:1 ratio, but in some cases the ratio may be 15 : 1 or otherwise, as when a club wheat and wheat with tapering head are crossed. In most cases the behavior can be explained on the basis of Mendel's law. Wheat hybrids are often fixed and many of the good commercial strains have originated in this way. No bud variations or mutations have been noted.

Mr. J. B. NORTON discussed the crosses which he and Mr. A. D. SHAMEL had made between wheat and rye. Wheat is always used as the mother parent, as rye refuses to set seed with foreign pollen. The first generation plants show great vigor, and though they resemble the mother at first, at blooming time the resemblance to rye increases until they would normally be mistaken for that plant. The hybrids are nearly sterile, as out of thousands of first generation flowers only three

produced viable seed, the plants from which were accidentally lost. In hybrids between tobacco varieties first generation uniformity and vigor are noticed in a marked degree.

In the case of oat hybrids Mr. Norton noted that the segregation in the second and later generations was normally Mendelian, though in one or two cases intermediate forms became fixed. There is a distinct coherence of characters shown when naked oats are crossed with the ordinary hulled type. Naked oats have more than three grains to the spikelet, while in hulled oats the spikelets are limited to two or three. The first generation gives a peculiar intermediate, while in the second the parent types reappear with the intermediates in a 1:2:1 ratio, showing complete coherence of the two pairs of characters. While this coherence has not been split, two strains of the intermediate type were fixed.

Of asparagus hybrids a peculiar case was mentioned. *Asparagus davuricus*, a Chinese species, when crossed with pollen of *Asparagus officinalis* gave a progeny that resembled in most characters the *A. davuricus* mother, with the exception of a greater vigor. The first generation plants dropped their branches in the fall like *A. davuricus*. These hybrids were crossed back with *A. officinalis*, but the second generation showed none of the abcission phenomena exhibited by their mother parent, although the expected ratio was 1 : 1. One of the first generation plants of this cross shows a vine-like habit, a character not present in either parent or in any close relative, although vining is common in other sections of the genus.

Dr. W. A. Orton discussed the behavior of disease resistance in hybrids, with special reference to the wilt diseases of cotton, okra, watermelons, and cowpeas, caused by the well-known vascular parasite belonging to the genus Fusarium.

In cotton, resistance which occurs in rare individuals is separated out by selection, and the crosses discussed were made between such resistant strains and other varieties of Upland cotton.

Certain conditions impair the exactness of results with reference to Mendelian ratios. The strains used were not of pure type and the most resistant show some disease; uniform exposure to infection is secured with difficulty; the severity of the disease varies with weather conditions. Susceptible plants are killed and their progeny are not available for further study.

In the first generation in cotton hybrids wilt-resistance is dominant, only a small percentage showing disease, usually less than that of the resistant parent. In the second generation there is a segregation of the wilt-resistant character and a large percentage of non-resistant plants are produced. In reciprocal crosses an effect from the female parent is apparent in the second generation. By selection from the resistant plants the selected third generation shows a marked increase in resistance.

In the cowpea wilt-resistance seems to be limited to a distinct variety, the Iron. In the first generation of crosses with other varieties wilt-

resistance is dominant. In the second generation about one-third of the plants were sterile, the percentage being as high as 73 in some hybrids. About 67 per cent of the plants were seed producing.

In the case of the watermelon, the citron or stock melon was used in breeding for a disease-resistant variety. In the first generation increased vigor was very noticeable, and in the second generation characters were noted which had not been noted before in either of the parents, particularly in the colors of the fruits, and also in a bitter taste not noted in either of the parents.

Mr. W. J. MORSE called attention to the behavior of hybrids in the soy bean, in which group study was made of the following characters: (1) flowers (white, purple); (2) pubescence (white, tawny); (3) seed (yellow, green, brown, black, bicolored); (4) cotyledons (yellow, green); (5) hypocotyl (green, purple); (6) smoothness; and (7) non-shattering. All of these are found to behave as Mendelian characters and to segregate according to Mendelian ratio. The only interrelation of characters noted is between the flower and the hypocotyl, the white flower being associated with the green hypocotyl and the purple flower with the purple hypocotyl. The non-shattering character is held to be one of the most important, and hybrids with this character have been fixed. Further work on this character with the standard commercial varieties is in progress. In the course of the hybrid work numerous sterile plants have been found. Natural hybrids of F_1 generation can usually be told in the field by the plants having a few smooth pods at the tip of the branches.

With the cowpea a large number of crosses have been made between the different commercial sorts, seeking to combine desirable characters. A study of the seed colors shows them to segregate in Mendelian ratio. Wilt and nematode resistance have been fixed in hybrids.

In the case of alfalfa, when hybrids of tender forms of *Medicago sativa*, such as Peruvian alfalfa, are made with *Medicago falcata* and the offspring subjected to severe winter conditions, there appears to be no tendency toward the elimination of the blue or purple-flowered forms, indicating that flower color is not particularly correlated with characters resulting in hardiness. There have been several crosses reported between rather distantly related species of Medicago, but it is believed that most of them are not true hybrids. It is believed that the *Medicago sativa* × *prostrata* hybrid is the only authentic one in the genus Medicago outside of the forms which Urban lists in his classification under *Medicago sativa*, which include *Medicago falcata* and *M. glandulosa*.

Mr. WALTER T. SWINGLE called attention to the great difference in the behavior of Citrus from other groups mentioned, in that a larger amount of variability occurred in the first generation of the hybrids. In Citrus many of these first generation hybrids are of commercial value and may be propagated without variation from seeds which contain usually only false embryos originating from the nucellar tissue of the mother plant. For example, hybrids secured between *Poncirus trifoliata* and the common orange, *Citrus sinensis*, are sterile, notwith-

standing which they produce an abundance of seeds. These seeds originate parthenogenetically and represent a pure strain of the female parent. But in some few cases there is a true second generation. The individuals of the first generation vary greatly. The fruit may be smaller than that of either parent, or larger than the combined fruits of the two parents; it may be smooth or hairy, lemon-colored or orange-colored, with a great profusion of oil glands or almost without any; the shape of the tree may vary; the leaves are often 5-foliolate, although one parent is unifoliolate and the other always 3-foliolate. There is a very considerable cohesion of characters in the second generation of Citrus-Poncirus hybrids. It seems all but impossible, however, to secure hardiness and an orange flavored fruit at the same time. In the case of Citrus-Poncirus hybrids great vigor is observed in the first generation. If this first generation is crossed with a kumquat, increased vigor also is shown; but no increase in vigor results from the return cross between the first generation and the parental species. The kumquat belongs to a distinct genus, Fortunella, so that in crossing a citrange with a kumquat a trigeneric hybrid is produced, combining Citrus and Poncirus with Fortunella. Although the kumquat is a dwarf plant, its diversity from Citrus and Poncirus is so great that when crossed with a citrange it brings about greatly increased vigor. By crossing *Poncirus trifoliata* with the ordinary orange, and then crossing this first generation hybrid with the kumquat, a fruit somewhat resembling the lime has been produced; it has no direct genetic relationship with the latter, however.

During the general discussion Mr. L. C. CORBETT and Prof. WILLIAM STUART discussed the behavior of carnation hybrids, and the latter called attention to the desirability of securing as high a percentage of germination as possible in the second generation, in order that no selective error be introduced into percentage determinations. Mr. NORTON said that of several thousand cases of carnations grown from commercial types, the percentage of singles never was higher than 23 per cent.

H. L. SHANTZ, *Corresponding Secretary.*